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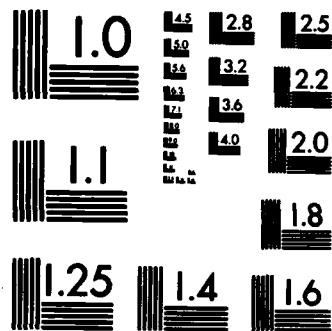
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Oxalate Ester Chemiluminescence, Improved Low Temperature Formulations

by
J. H. Johnson
H. P. Richter
D. J. Knight
R. A. Henry
Research Department

MAY 1985

NAVAL WEAPONS CENTER
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FOREWORD

This final technical report documents a study to reduce the effects of temperature change on the oxalate ester chemiluminescent reaction and to extend the effectiveness of the system to lower temperatures.

The work was accomplished under U.S. Army support, under Belvoir Research and Development Center MIPR Numbers A3285 and A4022 (Task A4415010121) for the period from July 1983 through September 1984.

The report was reviewed for technical accuracy by R. B. Green and A. L. Woodman.

Approved by
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Research Department
15 September 1984

Under authority of
K. A. DICKERSON
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Commander

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The objective of the program was to develop and test new chemiluminescent formulations which were usable at lower temperatures than the systems currently in use. The visibility requirements included a minimum visual range of 10 meters for 30 minutes at -25°F or lower. The oxalate ester-hydrogen peroxide chemiluminescent system was used. A series of new formulations were developed which offer reduced temperature sensitivity in a variety of colors. The formulations were tested at Ft. Greely, Alaska, where the program objectives were met and exceeded.

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We are indebted to Tom Basham and James Porterfield of the Belvoir Research and Development Center, Ft. Belvoir, Va., who supported us with funds and contributed to this program. The U.S. Army Cold Region Test Center, and specifically Capt. John Kincaid and his crew, did an outstanding job of laying out and running the field tests at Ft. Greely, Alaska. We wish to thank the American Cyanamid Company, Wayne, N.J., for supplying the empty glass ampoules and the plastic lightstick parts at no charge.

INTRODUCTION

The U.S. Army has developed track-width minefield clearing systems for assault armor units. A letter requirement for an improved day/night marking system for the cleared lane has been issued. The Cleared Lane Marking System (CLAMS) was designed to meet this requirement and the system is now being evaluated. A need for a more effective night marking system for CLAMS has been expressed. Various techniques including black paint, safety flares, and chemiluminescent (CL) lightsticks were tested. The lightstick was found to be the most promising nondevelopmental candidate to meet the night marking requirement. The lightstick is mounted on a 6-inch metal disk and is dispensed at variable distances by the CLAMS device. For night operations, the CLAMS visibility requirements include a minimum sighting distance of 10 meters for 30 minutes at temperatures ranging from -25 to +110°F.

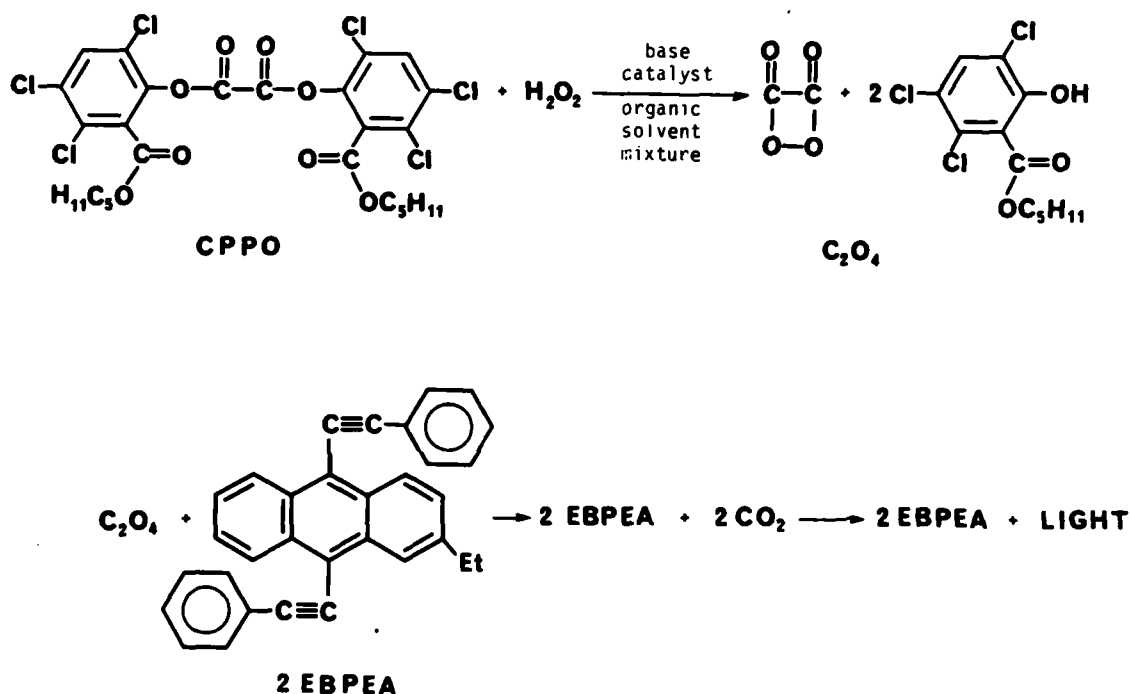
The Naval Weapons Center (NWC) was tasked in July 1983 to develop improved low-temperature formulations for the lightstick and to fabricate at least 200 units for evaluation at the U.S. Army Cold Region Test Center, Ft. Greely, Alaska, in January 1984. This relatively quick reaction program was undertaken with the intention of applying and further expanding upon the results of earlier U.S. Army and Marine Corps supported efforts at NWC (Reference 1). In those programs, the feasibility of using the oxalate ester CL system as the light source for night target or reference point marking was demonstrated. This new study addressed temperatures down to -48°F with a goal of meeting the CLAMS requirements at -25°F.

BACKGROUND

The oxalate ester/hydrogen peroxide CL reaction has been studied since 1962 with the majority of the research carried out by the American Cyanamid Company, Wayne, N.J., and by NWC. A steady increase in light capacity over these years brought this system up to a level of possible practical use in 1968 and since then most of the basic and applied CL research has been concentrated on this reaction. The system consists of two liquids which are stored separately and luminesce instantly when mixed. The intensity and duration of the

light emission can be varied by catalysis and the color of emitted radiation can be varied by dye selection from a family of fluorescent compounds. Light yields of 500 to 1000 lumen hours per liter are now attained with CL formulations. As a point of reference, a 60-watt incandescent light bulb operated at 115 volts emits 740 lumen and, therefore, 740 lumen hours in a period of 1 hour.

The CL reaction is illustrated by the following equations:



The oxidation of bis(2,4,5-trichloro-6-carbopentoxymethylphenyl)oxalate (CPPO) by hydrogen peroxide (H₂O₂) to give the dioxetanedione (C₂O₄) is catalyzed by weakly basic salts in organic solvents and the reaction is undoubtedly more complex than is shown here (Reference 2). The C₂O₄ intermediate, an unstable, energy-rich species, transfers chemical energy to the fluorescer 2-ethyl-9,10-bis(phenylethynyl)anthracene (2EBPEA) which is excited to its first electronic singlet state. The excited molecule then fluoresces with the emission of its characteristic color.

In practical use, two CL solutions are stored separately and mixed when light is required. Usually, three parts by volume of a solution of CPPO and fluorescer in the solvent dibutyl phthalate

(DBP) are mixed with one part by volume of an H_2O_2 solution. The H_2O_2 solution, as prepared from liquid 98% H_2O_2 , contains the dissolved basic salt catalyst for the reaction.

Earlier studies of this CL reaction had shown that the reaction slows down with decreasing temperature to give a lower intensity and an increased duration. This is, of course, what is normally observed in chemical reactions; however, the magnitude of the change with temperature can be controlled in some reactions. The primary goal of this effort then was to attempt to minimize this temperature effect and thereby improve the light output of the lightstick at low temperatures.

The American Cyanamid Company manufactures a number of lightsticks which vary in terms of size, color and duration of usable light. The National Stock Numbers (NSN) of those now available are listed in Table 1.

TABLE 1. Lightstick National Stock Numbers.

NSN	Description	Duration
6260 00 106 7478	4-inch, green	2 hours
6260 01 074 4230	6-inch, yellow green high-intensity	30 minutes
6260 01 074 4229	6-inch, green	12 hours

EXPERIMENTAL SECTION

LIGHT MEASUREMENTS

The light output of the CL formulations was measured by techniques which have been described in detail elsewhere (Reference 3). In general, the luminance of CL solutions in 1-centimeter cuvettes was measured with a narrow field of view photometer. The luminance, as measured in footlambert units, was converted to total luminous flux per unit volume by the formula

$$F = \frac{4.30 \cdot L \cdot n_D^2}{D}$$

where F is the flux in lumens per liter, L is the luminance in foot-lamberts, n_p is the refractive index of the solution, and D is the thickness of the cuvette in centimeters.

TEMPERATURE CONTROL CHAMBER

Light output measurements as a function of temperature were made in a small commercial freezer which was modified to include a glove port through which CL solutions were mixed by hand and poured into a light measuring cuvette, viewing ports through which the mixing process was viewed and the light output measured, and a temperature controller which allowed regulation to $\pm 1.0^\circ\text{F}$. The low temperature limit of the freezer was -26°F when the program was started and was lowered to -60°F during the program. A -60°F circulating cold bath was plumbed into the freezer to give faster cooling.

Premeasured samples of CL solutions were put into the chamber and temperature conditioned for a minimum of 60 minutes prior to mixing and testing. At the lower temperatures, where the solutions became more viscous, the mixed solution was poured back into the original sample vial to assure that all of the sample was mixed. In the case of commercial lightsticks, the stick was broken in the chamber by flexing and then rotating the stick end-for-end for approximately 30 seconds to mix the solutions. An end was then cut off the stick and the solution poured into a cuvette for measurement.

CL COMPONENT PREPARATION

The solvents used in the CL formulations were of special grade. Dibutyl phthalate and dimethyl phthalate (DMP) were purchased from Eastman Organic Chemicals, Rochester, N.Y., as "distilled grade for photographic use." 3-Methyl-3-pentanol (3M3P) was distilled twice prior to use. The compound CPPO was purchased from the American Cyanamid Company. Prior to use, CPPO was recrystallized twice from acetonitrile (melting point $181-189^\circ\text{F}$ ($83-87^\circ\text{C}$)). Concentrated H_2O_2 (98%) was purchased from the FMC Corp., Buffalo, N.Y. The fluorescent dyes 9,10-bis(phenylethynyl)anthracene (BPEA) and 1-chloro-9,10-bis(phenylethynyl)anthracene (ClBPEA) were purchased from the American Cyanamid Company. 2-Ethyl-9,10-bis(phenylethynyl)anthracene (2EBPEA) and 1,4-dimethyl-9,10-bis(phenylethynyl)anthracene (1,4DMBPEA) were prepared at NWC. The appendix includes the procedures used in the synthesis of 1,4DMBPEA. 5,6,11,12-Tetraphenylnaphthacene (Rubrene) was from the Aldrich Chemical Company, Milwaukee, Wis. Reagent grade compounds and solvents were used where available in the preparation and recrystallization of the lithium salt catalysts with the exception of lithium salicylate (LiSal) which was purchased as 99%+ purity from Gallard-Schlesinger Chemicals, Carle Place, N.Y.

The CL solutions were prepared by methods which were developed in an earlier program (Reference 4). In summary, the CPPPO solutions were prepared by first dissolving the oxalate ester in dibutyl phthalate at room temperature followed by heating of the solution to 302°F (150°C) in a covered beaker with constant bubbling of nitrogen and with stirring. The temperature was maintained at 302°F (150°C) for 1 hour with nitrogen purge and constant stirring. The solution was then allowed to cool to 122°F (50°C) at which time the fluorescent dye was added. The solutions were stored in Teflon fluorinated ethylene-propylene (FEP) bottles in the dark.

The H₂O₂ solutions were prepared by the slow addition with stirring of 98% H₂O₂ to the indicated solvent followed by the addition of the salt catalyst. These solutions were also stored in Teflon FEP bottles in the dark prior to use.

LIGHTSTICK FABRICATION

Two lots of approximately 250 lightsticks each were fabricated in-house for low temperature field testing. They contained new green and yellow formulations developed during the program.

The glass ampoules were loaded with 2.5 cubic centimeters of the hydrogen peroxide/catalyst solution and were sealed with a torch. The main body of the lightstick was then loaded with 7.5 cubic centimeters of the oxalate ester/fluorescer solution and the glass ampoule. The unit was then sealed by first heating the upper plastic surface of the tube to a molten state by contact with a hot plate held in an inverted position. The plastic cap, preheated to approximately 190°F, was then pressed into the tube to form the seal. The cap was then held in place with a clamp until cooled. The flashing bead, which extruded from the seal, was flattened by rotating the bead against the vertical edge of the hot plate to complete the seal.

LABORATORY STUDIES

APPROACH

The initial approach was to study the CL reaction variables as a function of temperature to determine which parameters were involved in the rate determining slow step of the reaction. This was a continuation of the studies begun earlier where it was found that the concentrations of the oxalate ester and hydrogen peroxide were not involved in the slow step and thus, a change in the concentration of either did

not affect the rate of the reaction (Reference 1). The effect of solvent viscosity on the reaction rate had also been determined earlier and no effect was observed. The catalyst and the fluorescers were thus the primary focus of this study.

The Cyalume® 30-Minute Hi-Intensity lightstick served as a baseline for the study. The light output-temperature profile of this formulation was studied early in the program and additional tests down to -48°F were made after the Ft. Greely field tests. The results are shown in Figure 1.

CATALYST EVALUATION

The most effective catalysts for the oxalate ester CL reaction include the carboxylic acid salts of the alkali metals, alkaline earths and the tetraalkylammonium cations. In an earlier program, the temperature effect and storage stabilities with hydrogen peroxide for the three classes were studied (Reference 1). The lithium carboxylic acid salts were shown to have a lower temperature dependence or lower activation energy than the others. That program was concluded prior to a thorough study of this family of catalysts. The study was resumed in this effort.

A series of lithium salts were evaluated in terms of solubility and catalytic activity in the solvent 3M3P. The solubilities were determined by flame emission spectroscopy. The results are shown in Table 2. The lithium salicylate, 5-t-butyl salicylate and 2-chlorobenzoate salts all looked promising and were evaluated further. Table 3 shows the results of temperature variation studies where the light yields, Q , were determined for various time periods after activation of the formulation. Q_{30} , for example, is the light yield during the first 30 minutes at the indicated temperature. Q_T is the total light output to a maximum time of 24 hours at low temperature. For comparison purposes, the same oxalate ester solution No. 206 (0.175 molar CPPO, 7.5×10^{-3} molar 2EBPEA in DBP) was used throughout the study. In comparing the results of Table 3, the lithium salts were still the most promising and of these, lithium salicylate was selected for the new formulation. This salt was chosen because of availability, cost, and the fact that work was done with it earlier.

Light output studies as a function of lithium salicylate concentration led to a final formulation for the hydrogen peroxide component. Solution No. 192 was formulated at 3×10^{-2} molar lithium salicylate, 1.5 molar hydrogen peroxide in the solvent 3M3P. This solution was used in most of the fluorescer studies discussed below and was used in both the new green and yellow lightsticks that were later tested at Ft. Greely.

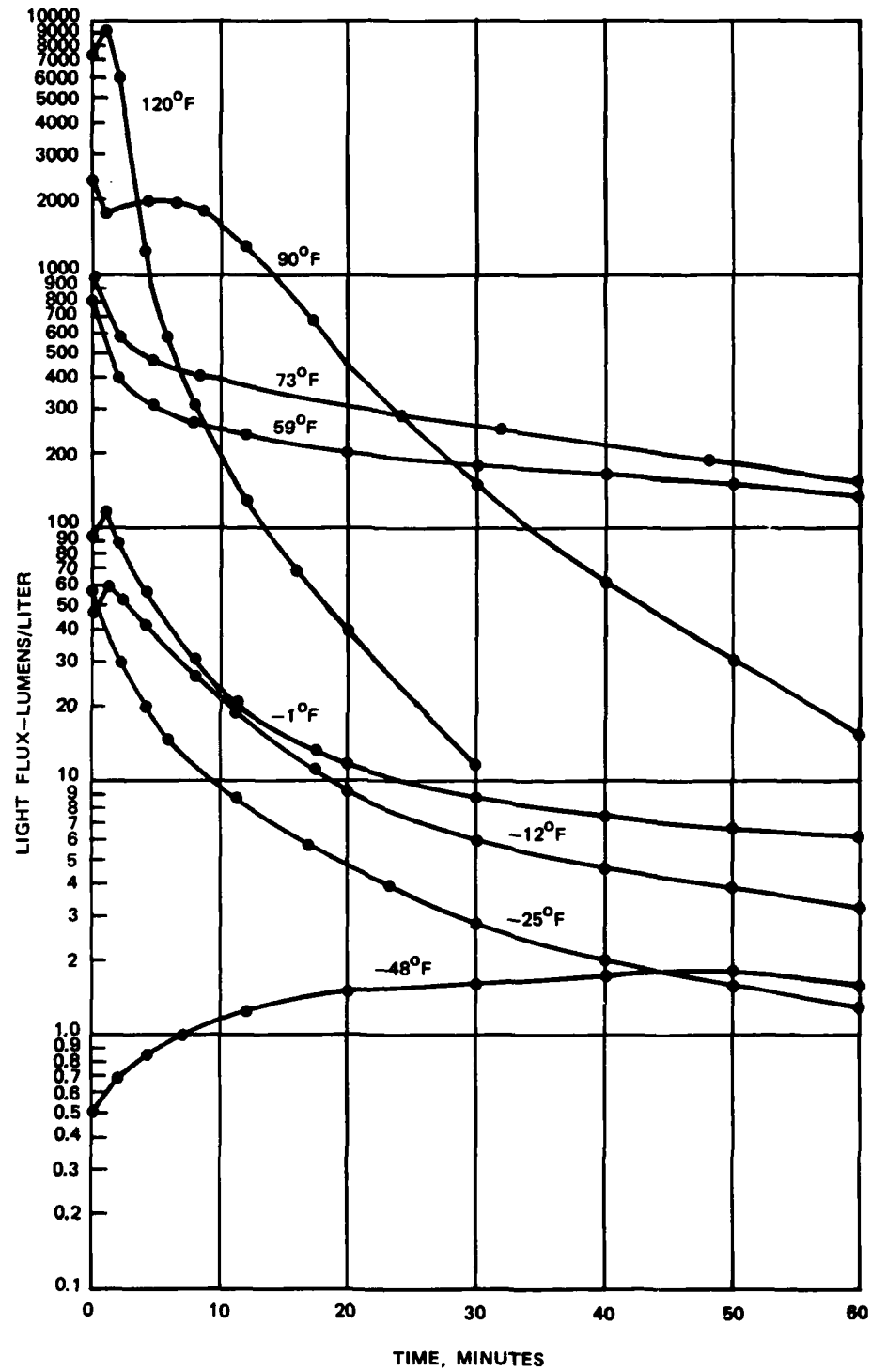


FIGURE 1. Light Output Variation With Temperature of the Cyalume® 30-Minute Hi-Intensity Lightstick.

TABLE 2. Solubility and Catalytic Activity of Lithium Carboxylic Acid Salts.

Salt	Solubility, parts per million ^a	Catalytic activity
Lithium salicylate	889	High
Lithium 2-chlorobenzoate	N/A ^b	High
Lithium 2,4-dihydroxybenzoate	151	High
Lithium 5-t-butylsalicylate	74	High
Lithium 2,2-dimethylpropionate	48	N/A
Lithium 5-octylsalicylate	35	N/A
Lithium 4-n-butoxybenzoate	5	N/A
Lithium lactate	7	Low
Lithium propionate	18	Low

^aThe indicated salt was added in excess to the solvent 3M3P and allowed to stand at 73°F for 7 days.

^bNot tested.

FLUORESCER EVALUATION

The approach used in this phase of the study was to optimize formulations of available fluorescent dyes for minimum temperature effect. The oxalate ester concentration was fixed at 0.175 molar based on the earlier work. At this concentration the ester remains in solution down to -20°F for extended periods of time. The LiSal catalyst solution No. 192 was used in most of these studies. The solubility of LiSal at -25°F appears to be higher than the 3×10^{-2} molar used in solution No. 192 as no precipitate was evident after -25°F storage for 30 days.

The available fluorescers were studied as a function of temperature and the results at -25°F are shown in Figure 2. Surprisingly, the fluorescer structure had a significant effect upon the reaction rate especially at lower temperatures. This suggests that the dye is directly involved in the slow, rate-determining step of the reaction. Thus, the slow step involves the fluorescer, the catalyst, and the dioxetanedione intermediate of the CL reaction. Again, our previous work indicated that the rate was independent of the ester and hydrogen peroxide concentrations as well as the solvent viscosity.

TABLE 3. Temperature Dependence of Oxalate Ester-Hydrogen Peroxide Chemiluminescence.

Catalyst and concentration ^a	73°F Q_{30} , Q_{60} , Q_T	32°F Q_{30} , Q_{60} , Q_T	-4°F Q_{30} , Q_{60} , Q_T	-25°F Q_{30} , Q_{60} , Q_T
Lithium salicylate 7.5×10^{-3} M	305, 320, 320	163, 201, N/A	93, N/A, N/A	26, 44, N/A
Lithium 5-t-butyl salicylate 7.5×10^{-3} M	310, N/A, ^c N/A	150, N/A, N/A	74, N/A, N/A	N/A
Lithium 2-chloro- benzoate 5×10^{-3} M	285, N/A, N/A	143, N/A, N/A	71, N/A N/A	N/A
Sodium salicylate 2.5×10^{-4} M	160, 291, 650	29, 45, 205	11, 14, 22	7, 8, 17
Cyalume® 30 Min. Hi-Intensity lightstick	180, 275, N/A	32, 51, N/A	10, 12, N/A	6, 7, N/A
Sodium trifluoro- acetate 1.25×10^{-2} M	590, 590, 590	176, 266, 410	20, 37, 211	4, 7, 110
Tetrabutylammonium salicylate 2.5×10^{-4} M	197, 342, 600	52, 73, 426	36, 46, 66	9, 17, 44

^aThe indicated catalyst concentration (final when mixed), was tested in a solution of 0.131 M bis(2,4,5-trichloro-6-carbopentoxypentyl)oxalate, 5.63×10^{-3} M 2-ethyl-9,10-bis(phenylethynyl)anthracene, 0.375 M hydrogen peroxide and a solvent mixture of dibutylphthalate with 3M3P or dimethylphthalate/t-butanol (DMP/t-BuOH).

^b Q_{30} is the light yield during the first 30 minutes after mixing, Q_{60} is 60 minutes after mixing, and Q_T is the total light output.

^cNot tested.

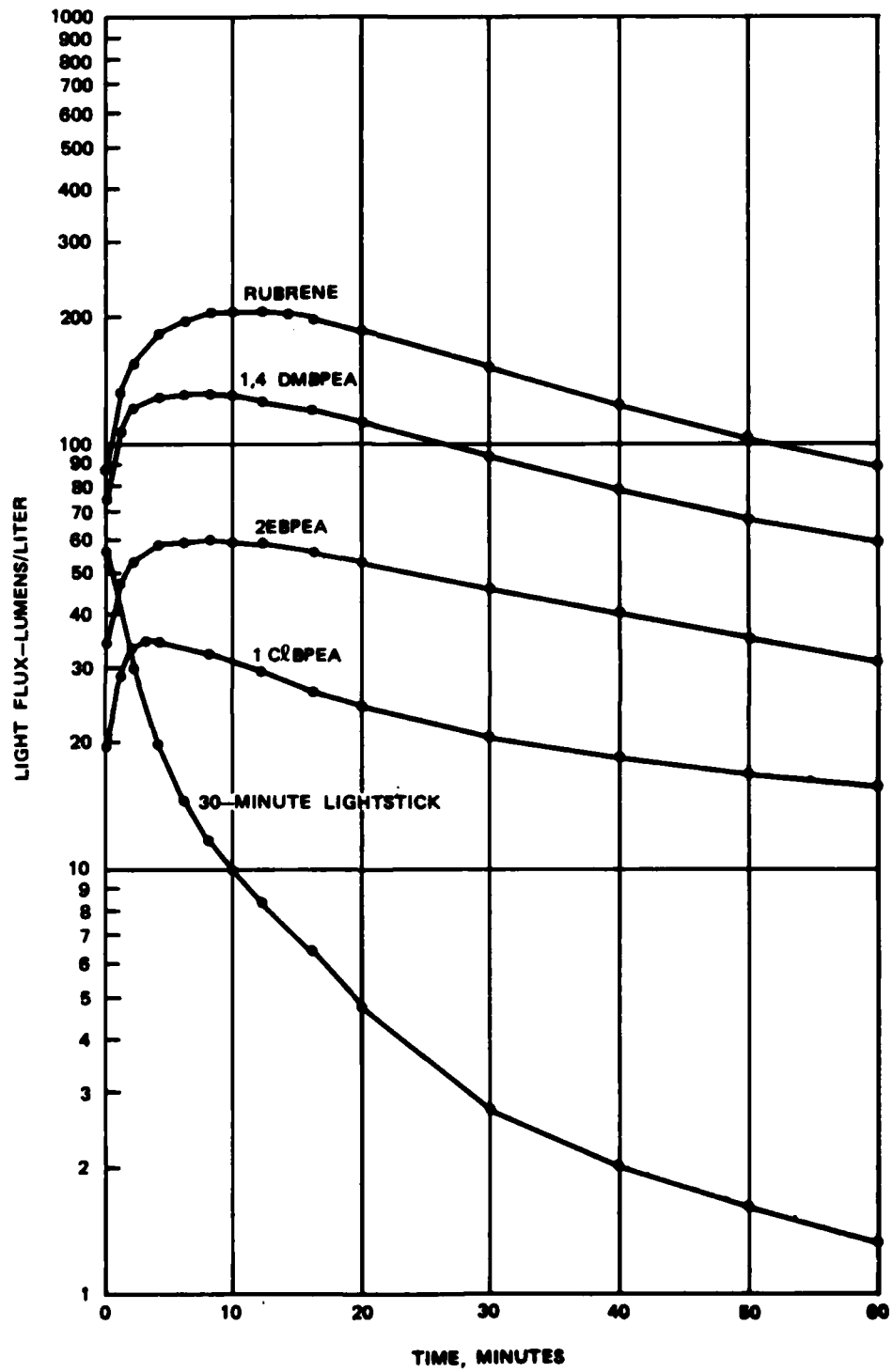


FIGURE 2. Fluorescer Studies at -25°F.

The results of Figure 2 also suggest an electronic effect in the fluorescer reaction rate: the electron-donating methyl and ethyl substituents on BPEA show increased rates, while the electron-withdrawing chloro group slows the reaction. BPEA, itself, was not included in the study due to poor solubility. The results with Rubrene, an orange emitting dye, showed the highest light levels of the group. Rubrene formulations, however, were not included in those tested at Ft. Greely because of a photo degradation problem with the dye.

FORMULATIONS

The CL formulations developed and characterized in the program are listed in Table 4. The overall formulation includes one part by volume of a hydrogen peroxide component and three parts by volume of an oxalate ester-fluorescer component.

TABLE 4. Chemiluminescent Formulations.

Solution No.	Composition
Hydrogen Peroxide Components	
192	1.5 M H ₂ O ₂ , 3 x 10 ⁻² M LiSal in 3M3P
212	1.5 M H ₂ O ₂ , 4 x 10 ⁻³ M sodium salicylate (super saturated), 0.10 M sodium trifluoroacetate in 80/20 volume percent DMP/t-BuOH
Oxalate Ester-Fluorescer Components	
205	0.175M CPPO, 7.5 x 10 ⁻³ M Cl BPEA in DBP
206	0.175M CPPO, 7.5 x 10 ⁻³ M 2EBPEA in DBP
207	0.175M CPPO, 6 x 10 ⁻³ M 1,4DMBPEA in DBP
209	0.125 M CPPO, 3 x 10 ⁻³ M Rubrene in DBP
214	0.175 M CPPO, 3 x 10 ⁻³ M 2EBPEA in DBP

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From these studies, two formulations were selected to be loaded into lightsticks for the field tests. A green emitting formulation consisting of solutions No. 206 and 192 and a yellow formulation of solutions No. 207 and 192 were chosen. The light output as a function of temperature and time was measured for both formulations and the results are shown in Figures 3 and 4.

FIELD TESTS

PRELIMINARY FIELD TESTS AT NWC

The CLAMS marking requirement for the lightstick includes a minimum visibility of 10 meters for 30 minutes through the periscope of a tank. In order to determine the light flux level that was necessary to meet the requirement, a visibility test was conducted on the NWC ranges. Two 30-Minute Hi-Intensity lightsticks were placed 10 meters in front of an M-41 tank. The lightsticks were activated and placed on stands 22 inches above ground level and 8 inches apart. Under these conditions they were considered as separate light sources. The tank faced north where there were no background lights and the night sky was very dark and overcast. The observer's eyes were dark-adapted for 30 minutes prior to the start of the test.

The ability of three observers to see the lights through the periscope was monitored as a function of time after lightstick actuation. The temperature was also monitored. After 5 hours, the lightsticks were still easily seen through the periscope. The lightsticks were then moved out to a distance of 100 meters where they were still visible. The average temperature during the test was 59.5°F and varied from 59 to 62°F.

The field temperature conditions were reproduced in the laboratory and the lightstick light output as a function of time was measured over a period of 5 hours. The flux at 5 hours was 22.8 lumens per liter, and, again, the field tests showed that at 10 meters the lightstick was easily seen at this light level. The distance squared relationship when applied to the 100-meter test suggests that a flux level of 0.228 lumen per liter would meet the CLAMS requirement when very dark overcast sky conditions are present.

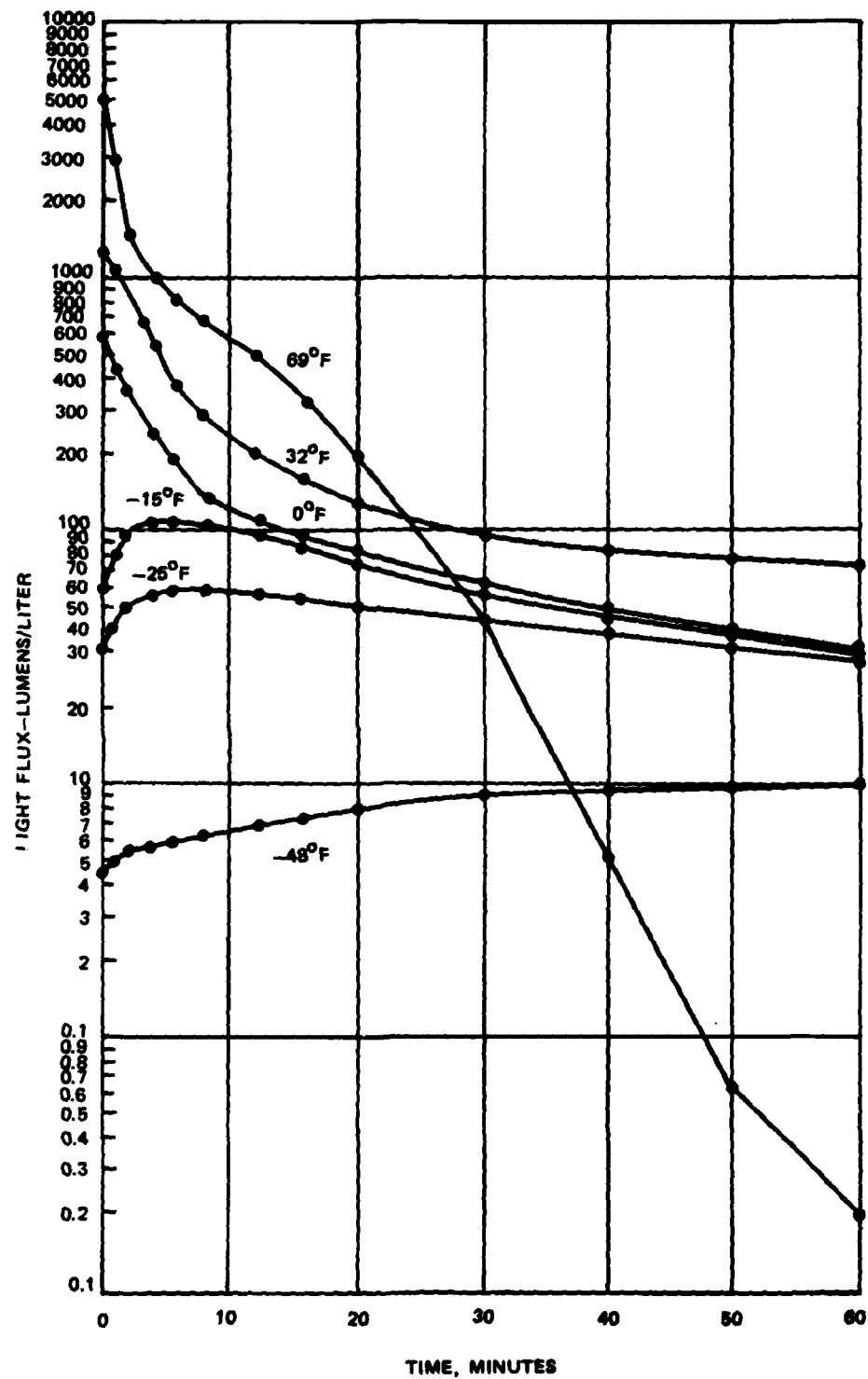


FIGURE 3. Green Formulation (Solutions No. 206 and 192)
Light Output Variation With Temperature.

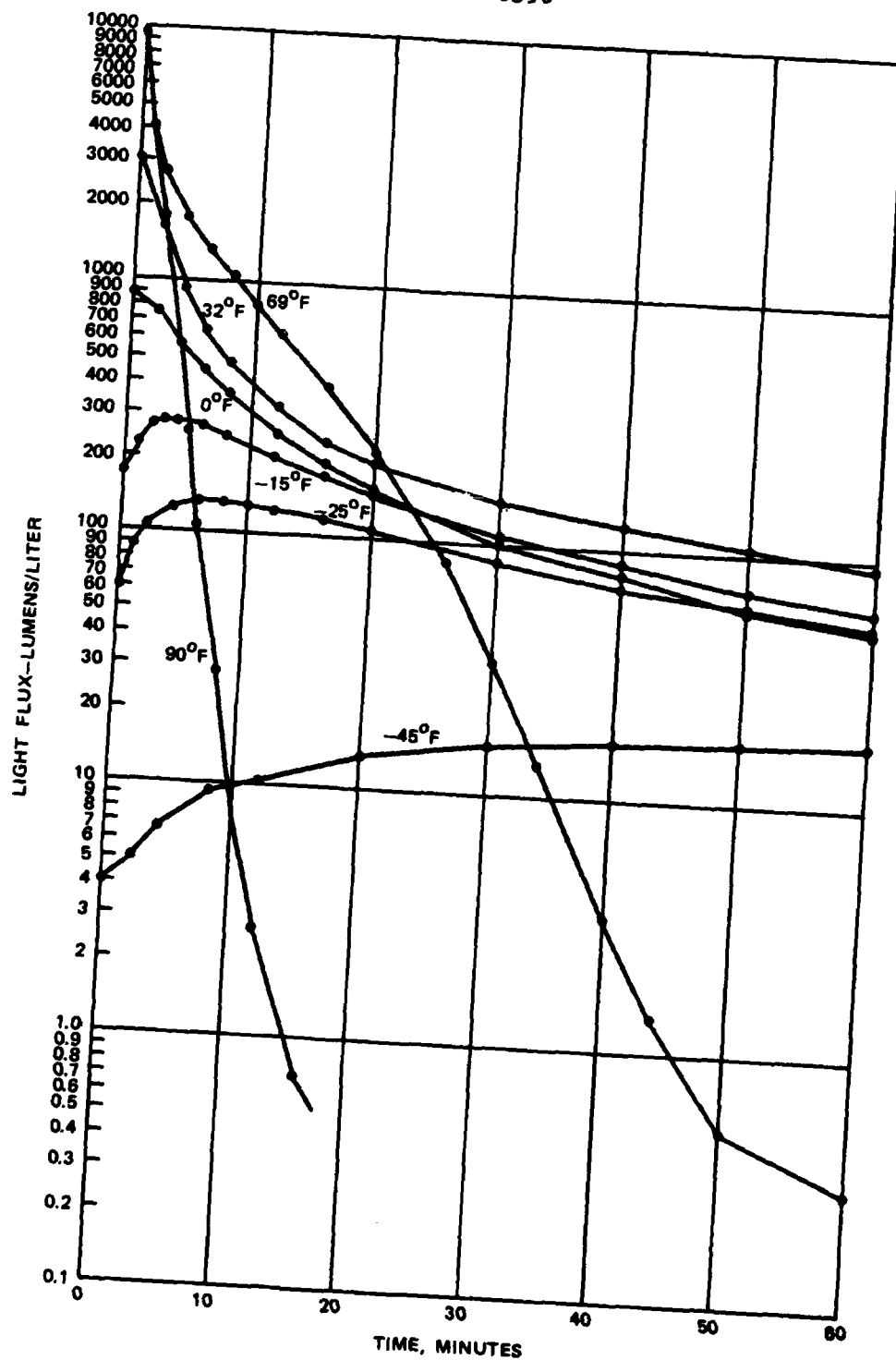


FIGURE 4. Yellow Formulation (Solutions No. 207 and 192)
Light Output Variation With Temperature.

FT. GREELY FIELD TESTS

A series of night field tests were conducted in February 1984 at the U.S. Army Cold Regions Test Center, Ft. Greely, Alaska, which is located 100 miles south of Fairbanks, Alaska. The tests were designed to assess the performance of the commercial 30 Minute Hi-Intensity lightstick and other lightsticks loaded with the new NWC formulations. Tests of the ability of a tank driver to traverse a lightstick-marked trail at -25°F was the primary goal. The lightsticks were to be placed 6 meters apart over a 250-meter, slightly curved trail, and the driver was to follow the trail at a speed of 5 to 10 miles per hour. If the driver ran over two or more markers, the breach would be considered a failure. The test plan was prepared by the Belvoir Research and Development Center, Ft. Belvoir, Va. NWC provided 200 each of the new green and yellow experimental lightsticks and 300 of the Cyalume® 30-Minute Hi-Intensity lightsticks. Two NWC personnel participated in the test.

The first night's test was designed to acquaint the participants with the test procedure. The conditions included a relatively warm temperature of -1 to -2°F with clear starlight and no moon. We decided to lay out a course of 30-Minute lightsticks to give the soldiers practice in breaking and mixing the lightsticks and in laying out the trail. The tank driver had no difficulty traversing the trail. Table 5 summarizes the results of the night's testing. When first activated, the lightsticks could be seen at 200 to 250 meters and the distance decreased down to 50 to 70 meters after 60 minutes. Two nights later, with the temperature at -11.2°F , the same lightsticks could be seen at 40 meters. The temperature the following evening was only -2 to -5°F and we decided to wait for colder weather.

TABLE 5. First Night Ft. Greely Test Results.

Lightstick	Distance observed, ^a meters	Time observed ^b	Time to breach	Markers run over	Temperature, °F
30-min	200-250	0 min	1 min, 55 s	0	- 1.2
30-min	100-150	30 min	3 min, 6 s	0	- 1.2
30-min	50-70	60 min	-	-	- 1.2
30-min	40	48 h	-	-	-11.2

^aDistance the lightstick could be seen.

^bElapsed time after lightstick activation.

On the third night testing was resumed. On returning to the test area, the team observed that the lightsticks actuated 48 hours earlier were still visible at approximately 40 meters. The same course as used on the first night was laid out again. The standard 30-Minute lightsticks were used again; they were more difficult to mix at the lower temperature. It was snowing lightly, but the visibility with overcast starlight seemed to be as good as on the first night. The test results are shown in Table 6. Although, the temperature was about 10°F colder than the first night, there was little difference in the test results. After 1 hour the 30-Minute Hi-Intensity lightsticks could still be seen at 70 meters. Photographs were taken by day (Figure 5) and during the night (Figure 6) of the same scene.

TABLE 6. Third Night Ft. Greeley Test Results.

Lightstick	Distance observed, ^a meters	Time observed ^b	Time to breach	Markers run over	Temperature, °F
30-min	200-250	0 min	1 min, 25 s	0	-11.2
30-min	100-150	30 min	1 min, 35 s	0	-11.8
30-min	70	60 min	-	-	-12.8
30-min	40	12 h	-	-	-22.0

^aDistance the lightstick could be seen.

^bElapsed time after lightstick activation.

On the fourth night, the weather had turned much colder with temperatures ranging from -45 to -49°F during the test period. Separately marked trails were laid out with all three lightsticks. The lightsticks were difficult to mix and it took some time to set up the marked trails. The weather was clear and dark with starlight and no moon. Occasional fog was caused by the exhaust of the vehicles which were left running. The test results are shown in Table 7. All the lightsticks met or exceeded the stated CLAMS requirement under these conditions. Even after 12 hours, the 30-Minute lightsticks were visible at 30 meters and the NWC yellow lightsticks were visible at 70 meters.

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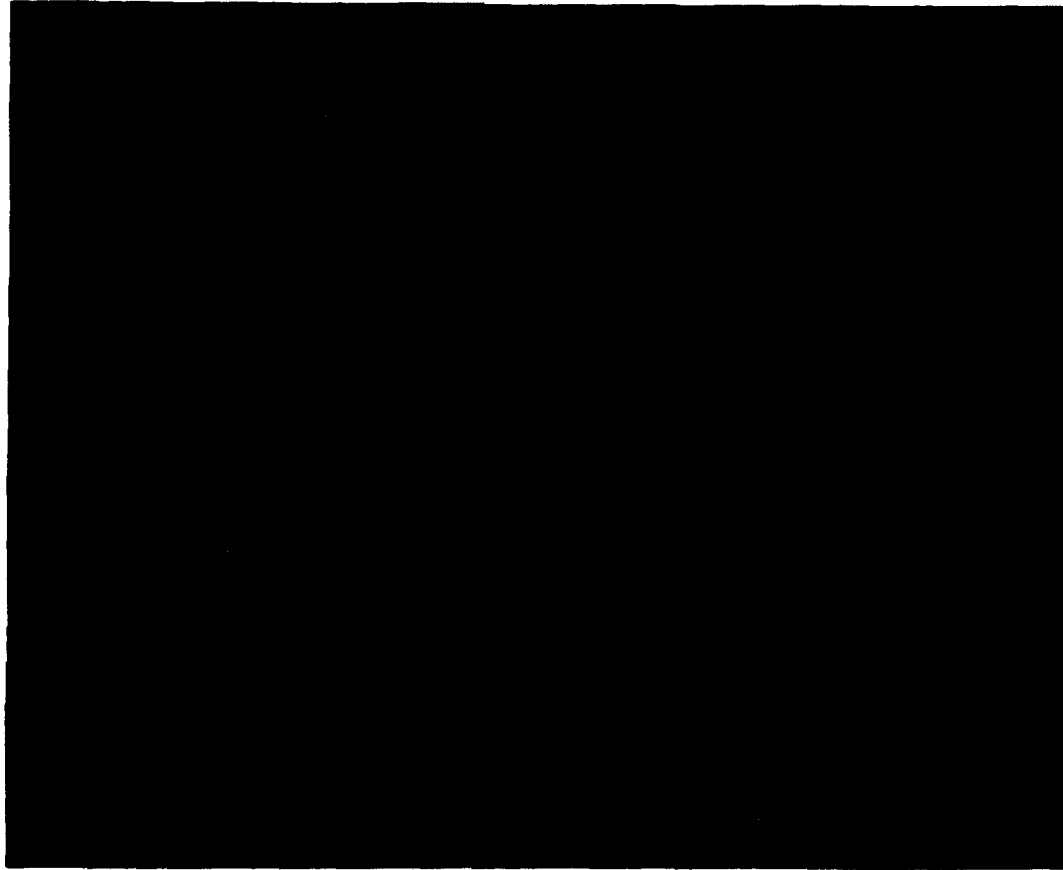


FIGURE 5. Test Area During Daylight Hours.

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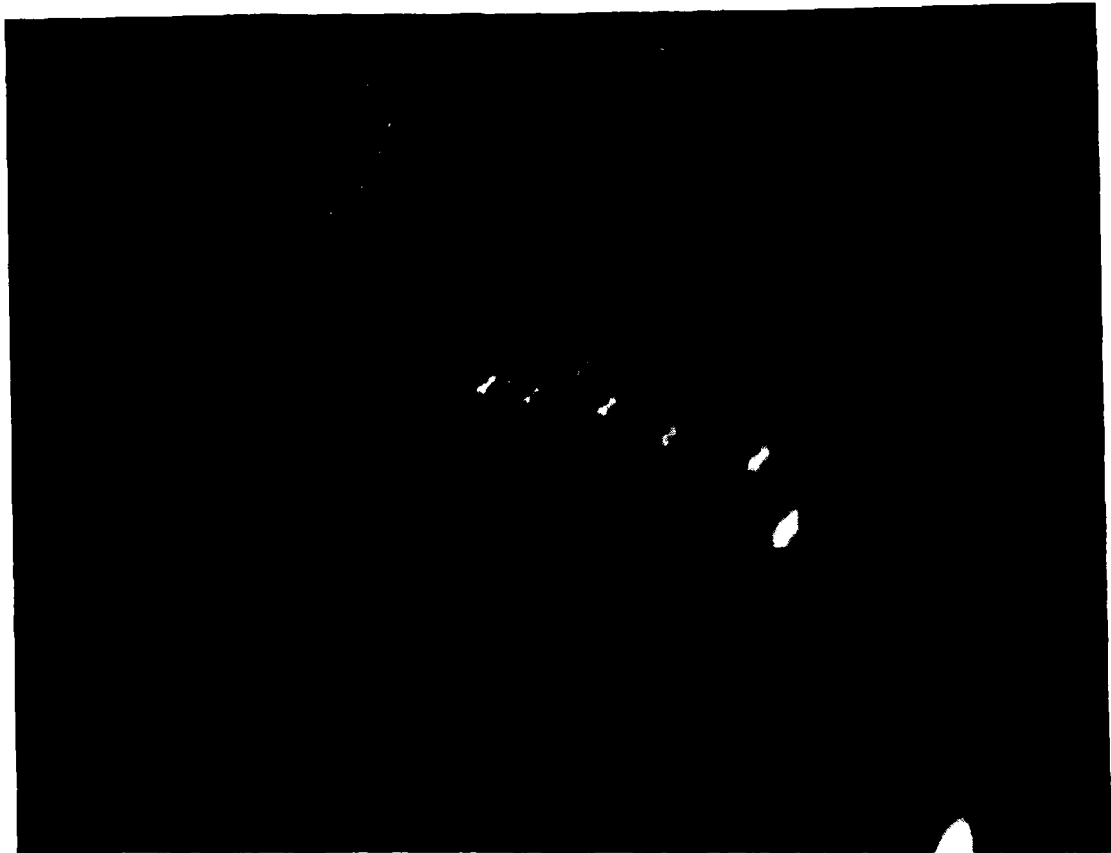


FIGURE 6. Test Area as Seen During the Test at Night.

TABLE 7. Fourth Night Ft. Greely Test Results.

Lightstick	Distance observed, meters ^a	Time observed ^b	Time to breach	Markers run over	Temperature, °F
30-min	70	0 min	1 min, 28 s	0	-46.7
30-min	40	30 min	1 min, 15 s	0	-48.5
30-min	40	60 min	-	-	-49.0
30-min	30	12 h	-	-	-45.4
NWC green	100	0 min	1 min, 25 s	0	-46.7
NWC green	70	30 min	0 min, 55 s	0	-48.5
NWC green	70	60 min	-	-	-49.0
NWC green	60	12 h	-	-	-45.4
NWC yellow	150	0 min	1 min, 10 s	0	-48.5
NWC yellow	100	30 min	1 min, 0 s	0	-49.0
NWC yellow	100	60 min	-	-	-49.0
NWC yellow	70	12 h	-	-	-45.4

^aDistance the lightstick could be seen.

^bElapsed time after lightstick activation.

POST FIELD TEST STUDIES

Additional laboratory studies were conducted after the Ft. Greely tests to measure the light output of the three lightstick formulations at the temperatures encountered in the field tests. Our equipment had to be modified to get down to -48°F. By using a dry-ice-ethanol bath, plumbed into the freezer coils, we were able to lower the freezer temperature to -60°F. The -48°F temperature was difficult to control and the actual temperature was $\pm 2^\circ\text{F}$ during these tests.

The three formulations evaluated at -1, -12, and at -48°F are shown in Figures 7 through 9, respectively. The yellow formulation is approximately 4 to 8 times brighter than that of the 30-Minute lightstick at all temperatures. The green is approximately 2 to 5 times brighter. The gain in visual acquisition range will increase as the square root of these values; thus, a factor of 4 increase in brightness will double the visual sighting range.

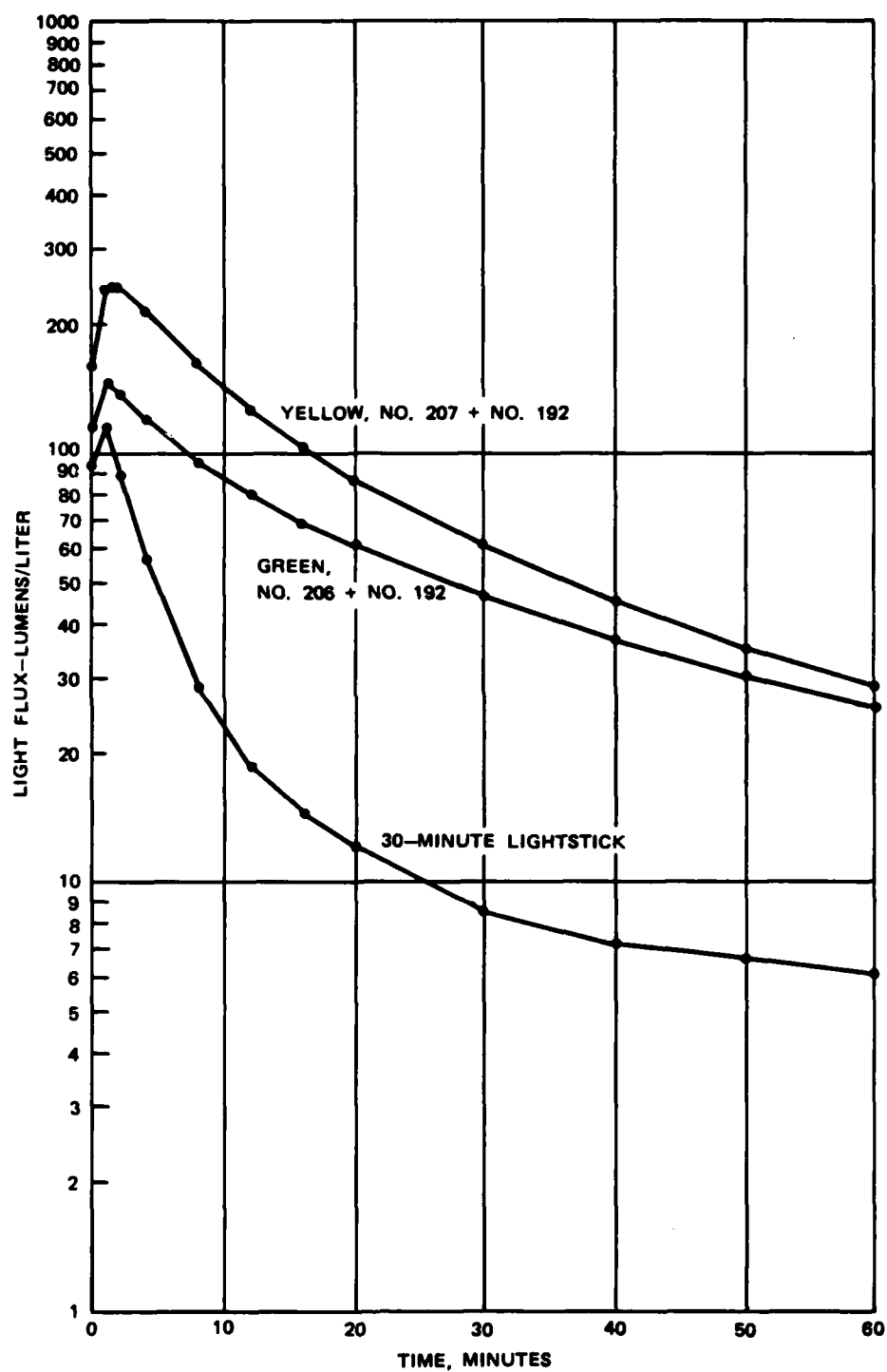


FIGURE 7. Formulation Light Output at -1°F.

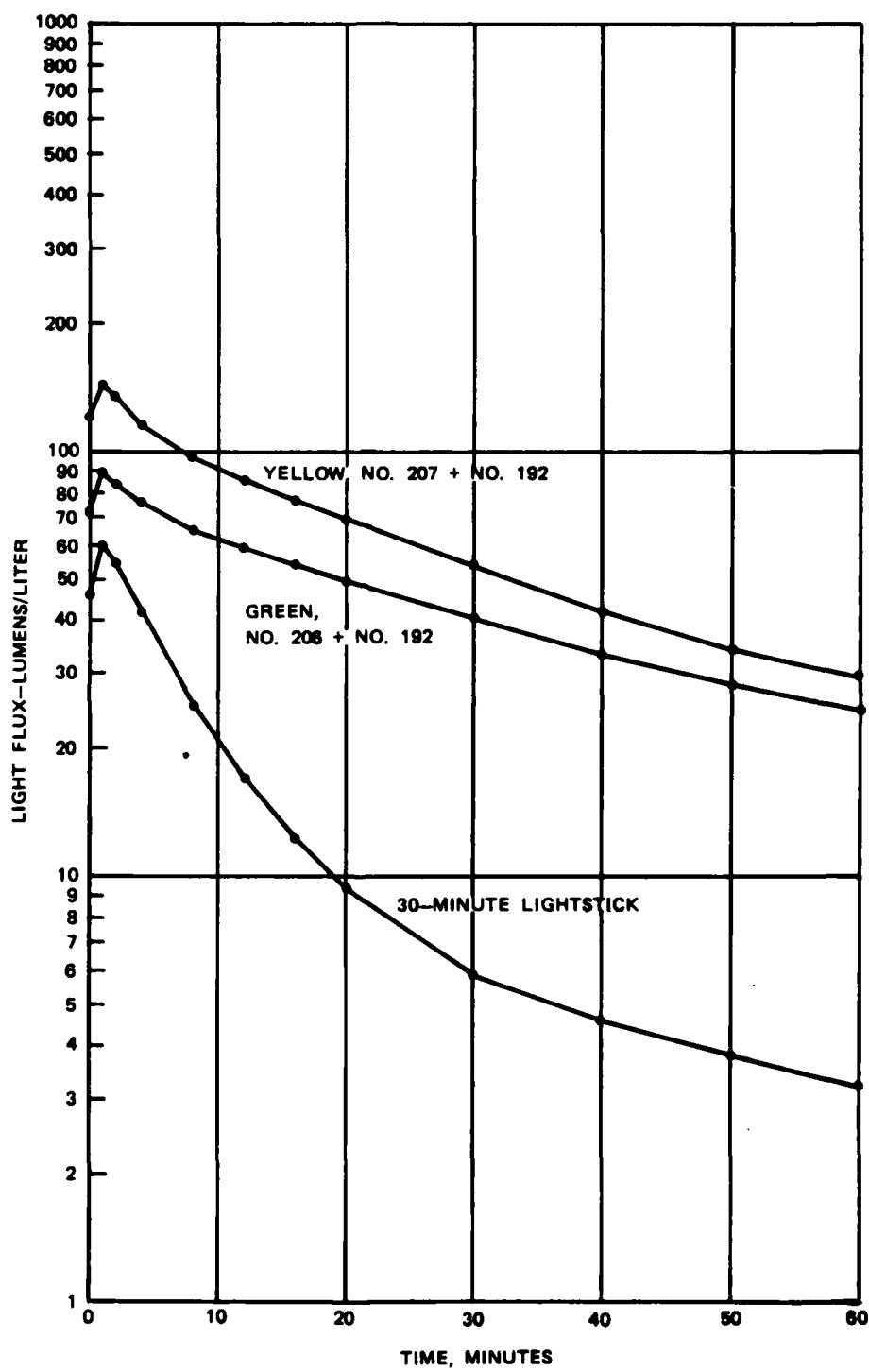


FIGURE 8. Formulation Light Output at -12°F.

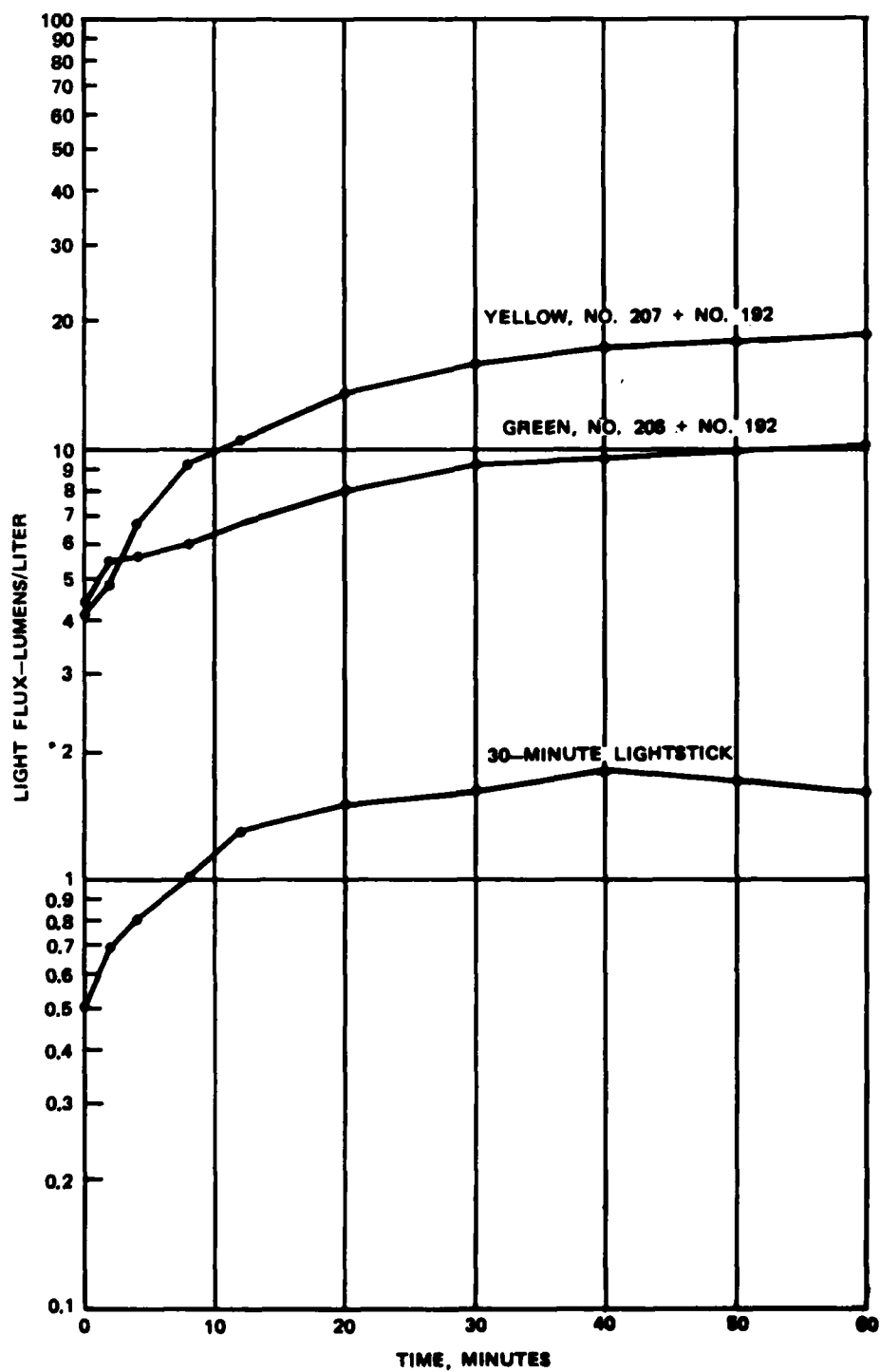


FIGURE 9. Formulation Light Output at -48°F.

PREDICTED VISUAL RANGES

Both the Ft. Greely and the NWC field tests were conducted during no-moon conditions where the dark background conditions gave maximum visual acquisition ranges. Predicted visual ranges can be determined (95% probability of detection) for other background illumination conditions as a function of the lightstick light output. The visibility nomographs of Middleton (Reference 5) were derived from extensive World War II studies of the visual acquisition range of circular luminous objects. The nomographs relate background luminance, contrast ratio, the size of the luminous object and the meteorological visibility range to predict visual acquisition ranges.

The nomographs were used in this study to calculate the minimum temperature at which the three formulations would meet the 10-meter CLAMS visibility requirement for 30 minutes duration.

Based on the NWC field test, a contrast ratio of 71 was calculated as the minimum value that will meet the CLAMS range through a tank periscope. The contrast ratio, C, was calculated as:

$$C = \frac{L_S - L_B}{L_B}$$

where L_S is the surface luminance of the lightstick and L_B is the background luminance, both in footlambert units. The lightstick luminance was calculated using

$$L_S = \frac{F \cdot V}{4\pi A}$$

which reduces to:

$$L_S = 0.303F$$

when values of 0.008 liter and 0.021 square feet are substituted for the volume, V, and projected surface area, A, of the lightstick. F is the light flux in lumens per liter of formulation at a specific temperature. The F values as a function of time and temperature for the three formulations were given in Figures 1, 3, and 4.

Table 8 shows the minimum temperatures at which the three formulations should meet the CLAMS requirements as a function of background illumination. All three will meet the requirements under quarter moon conditions or darker with minimum temperatures all below -25°F. Under full moon conditions, the 30-Minute formulation will not be effective at temperatures below 30°F while the two new formulations will exceed the -25°F requirement. Under twilight background conditions, all three formulations must be at 69 to 70°F and, even then, the green and yellow formulations burn out after 16 and 20 minutes, respectively.

TABLE 8. Minimum Effective Temperatures for CLAMS Visibility Requirements.

Atmospheric background illumination	L_B (fL) ^a	L_S (fL) ^b	F_{min} (lm^{-2}) ^c	Minimum effective temperature ^d		
				30-Minute	NWC green	NWC yellow
Overcast starlight	1×10^{-5}	7.2×10^{-4}	0.023	<-48°F	<-48°F	<-48°F
Starlight	1×10^{-4}	7.2×10^{-3}	0.23	<-48°F	<-48°F	<-48°F
Quarter moon	1×10^{-3}	7.2×10^{-2}	2.3	-30°F	<-48°F	<-48°F
Full moon	1×10^{-2}	7.2×10^{-1}	23.0	+30°F	-37°F	-40°F
Twilight	1×10^{-1}	7.2	230.0	+70°F	+69°F (16 min)	+69°F (20 min)

^aBackground luminance in footlamberts.

^bLightstick surface luminance.

^cMinimum formulation flux which will meet CLAMS visibility requirements.

^dThe minimum temperature at which the formulation yields F_{min} for 30 minutes.

SUMMARY AND CONCLUSIONS

A series of oxalate ester CL formulations were developed which give improved light output over a broad temperature range. The improved formulations will extend the visual acquisition range of a given CL system as well as lower the useful temperature limit. The new systems could be utilized in lightsticks as well as night marking or signaling devices.

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The Ft. Greely cold weather field tests demonstrated the feasibility of using a lightstick to mark the cleared lane through a minefield. The Cyalume® 30-Minute Hi-Intensity lightstick and lightsticks loaded with two new NWC formulations exceeded the CLAMS marking requirements at -48°F under dark, no-moon, conditions. Calculated visual acquisition range results indicate that, under full moon conditions, the new formulations will be required to meet the CLAMS requirements.

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Appendix

**REACTION STEPS IN SYNTHESIS OF 1,4-DIMETHYL-9,10-
BIS(PHENYLETHYNYL)ANTHRACENE**

1,4-Naphthoquinone (practical grade; 25 grams, 0.108 mole) and 15 grams (0.183 mole) of trans,trans-2,4-hexadiene were mixed with 50 milliliters of ether and 100 milliliters of absolute ethanol. The tightly stoppered flask stood at room temperature for 10 days; the contents were swirled occasionally. All of the quinone dissolved after about a week. The solution was diluted with 400 milliliters of 95% ethanol containing 25 grams of 85% potassium hydroxide, then refluxed for 8 hours while a stream of air was bubbled through. After cooling overnight at 41°F (5°C), the solid product was filtered, washed three times with cold ethanol (just enough to cover the cake), then washed repeatedly with water until free of base, and finally washed once more with cold ethanol. The yield of dried 1,4-dimethyl-9,10-anthraquinone was 31.4 grams (83%). A portion (6.8 grams) was recrystallized by solution in 500 milliliters of 95% ethanol, filtering through a Celite mat to decolorize and cool; the recovery of dark orange, flat needles was 6.1 grams, melting point 286-288°F (141-142°C), melting point found in the literature 140-141°C (Reference 6).

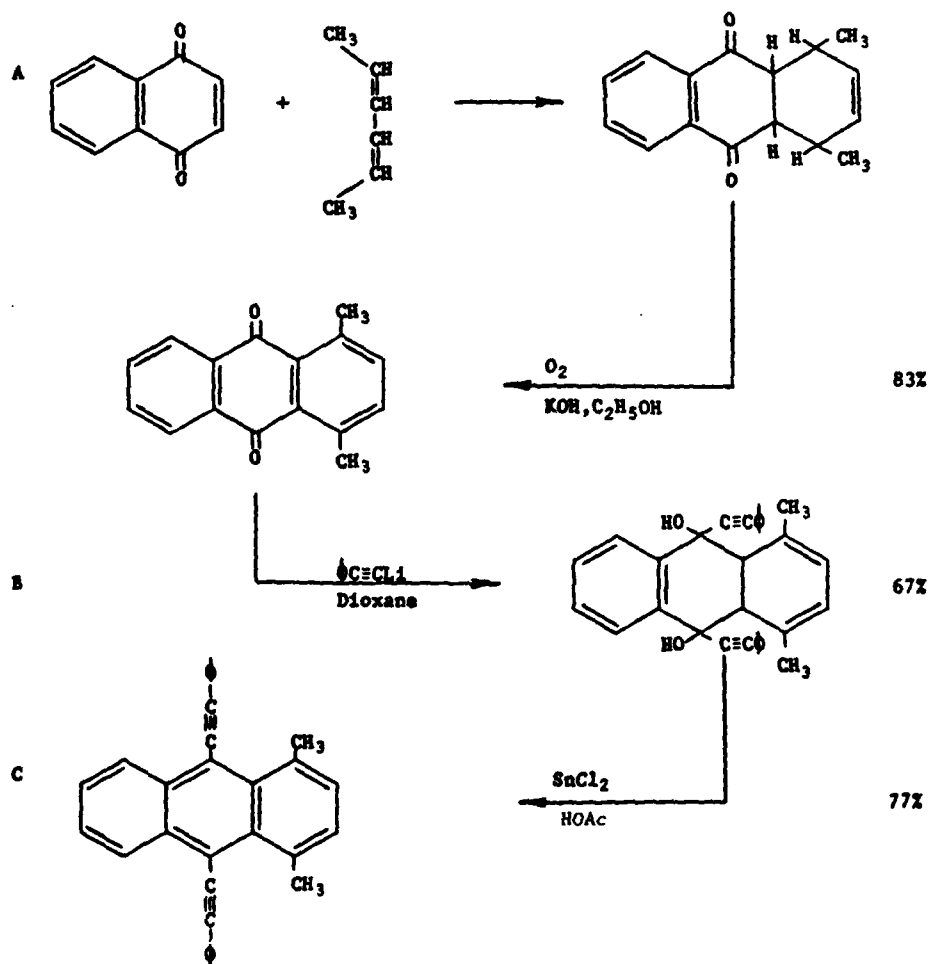
Phenylacetylene (13.0 grams, 0.127 mole), lithium amide (2.9 grams, 0.126 mole), and 200 milliliters of anhydrous dioxane were refluxed and stirred in a nitrogen atmosphere for 2 hours. After the solution had been cooled, dried 1,4-dimethyl-9,10-anthraquinone (13.3 grams, 0.051 mole) was added in one portion. Refluxing and stirring, still under nitrogen, were resumed and continued for 16 hours. Most of the dioxane was removed under reduced pressure. The cooled residue was stirred with 6.5 grams of ammonium chloride in 200 milliliters of water, heated to 122°F (50°C), recooled to room temperature, and then filtered; the crude anthradiol was washed well with cold water, twice with pentane, then vacuum dried at 158°F (70°C), 25 millimeters for 24 hours. (Since the anthradiol forms a 1:1 complex with dioxane, vacuum drying is essential to destroy this complex; otherwise, the subsequent recrystallizations are less satisfactory.) The yield was 24.6 grams, melting point 320-338°F (160-170°C). Recrystallization from 150 milliliters of benzene gave 16.7 grams (67%) of a mixture of epimers of 1,4-dimethyl-9,10-bis(phenylethynyl) 9,10-anthradiol, melting point 392-400°F (200-204°C); the infrared spectrum revealed no carbonyl absorption. (Evaporation of the benzene mother liquors left 7.8 grams of a mixture of anthradiol and the monodiol). Another recrystallization (not essential for the next step) raised the melting point to 400-405°F (204-207°C).

Analysis calculated for $C_{32}H_{24}O_2$: C, 87.24; H, 5.49. Found: C, 87.25; H, 5.50.

A solution consisting of 28.3 grams (0.125 millimole) of stannous chloride dihydrate in 220 milliliters of 50% aqueous acetic acid was stirred and flushed with nitrogen for 1 hour. Then 16.7 grams (0.038 mole) of the anthradiol in 180 milliliters of acetone was added

dropwise with stirring during 20 minutes. The reaction flask was protected from light. After being stirred overnight at room temperature under nitrogen, 4.5 grams of Celite was added and the slurry filtered. The cake was washed with water until free of acid, vacuum dried (25 milliliters) at ambient temperature, and then at 158°F (70°C). The dried cake was extracted with 350 milliliters of boiling benzene, while the solution was protected from light. Cooling the extracts to 41°F (5°C) furnished 10.4 grams of orange crystalline solid, melting point 345-348°F (174-176°C). A second crop of 1.2 grams was recovered by diluting the mother liquors with 300 milliliters of n-pentane and cooling to 5°F (-15°C). The total yield was 77%. Recrystallization of a portion from benzene raised the melting point to 348-350°F (176-177°C).

Analysis calculated for $C_{32}H_{22}$: C, 94.54; H, 5.46. Found: C, 94.24; H, 5.70.



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